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(21) International Application Number: PCT/GB97/01902 (22) International Filing Date: 14 July 1997 (14.07.97) (30) Priority Data: 9614967.9 17 July 1996 (17.07.96) GB (71) Applicant (for all designated States except US): THE UNIVERSITY OF BIRMINGHAM [GB/GB]; Edgbaston, Birmingham B15 2TT (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): DONG, Hanshan [CN/GB]; Flat 49, Griffin Close, Birmingham B31 2UY (GB). BLOYCE, Andrew [GB/GB]; 7 The Tynes, Bromsgrove, Worcestershire B60 3QQ (GB). MORTON, Peter, Harlow [GB/GB]; 18 Barnbrook Road, Knowle, West Midlands (GB). BELL, Thomas [GB/GB]; St. Mawes, 1 Mariners Road, Blundellsands, Merseyside L23 6SX (GB). (74) Agents: PEARCE, Anthony, Richmond et al.; Marks & Clerk, Alpha Tower, Suffolk Street Queensway, Birmingham B1 1TT (GB).		(81) Designated States: CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: SURFACE OXIDATION OF A TITANIUM OR TITANIUM ALLOY ARTICLE (57) Abstract The tribological behaviour of a titanium or titanium alloy article is improved by gaseous oxidation of the article at a temperature in the range of 500 to 725 °C for 0.5 to 100 hours, the temperature and time being selected such as to produce an adherent surface compound layer containing at least 50 % by weight of oxides of titanium having a rutile structure and a thickness of 0.2 to 2 µm on a solid solution-strengthened diffusion zone wherein the diffusing element is oxygen and the diffusion zone has a depth of 5 to 50 µm.		

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SURFACE OXIDATION OF A TITANIUM OR TITANIUM ALLOY ARTICLE

This invention relates to a process for the surface treatment of titanium and titanium alloys for the purpose of improving the tribological properties thereof, and also relates to surface-treated titanium and titanium alloys having improved tribological properties and uses for such surface-treated titanium and titanium alloys.

Over the past forty years, there have been many investigations into the effect of surface treatment of titanium and titanium alloys on surface hardness. A great deal of work has been devoted to the study of oxidation of titanium and its alloys which is generally viewed as a problem when surface treating titanium and its alloys in various gaseous environments. Little attention has been paid to the deliberate oxidation of titanium alloys for use as a tribological surface treatment. Investigations have been reported in various journals over a long period of time. H.W. Worner in "Surface Hardening of Titanium", The Australasian Engineer, November 1950, pages 52 to 55, observed that, when commercially pure titanium was heated in the range of 850 to 1000°C in air at a pressure of between 10^{-3} mm and 10^{-2} mm Hg, the surface was effectively hardened. However, R.W. Hanzel in "Surface Hardening Processes for Titanium and its Alloys", Metal Progress, March 1954 pages 89 to 96 discounted the commercial utility of such process since, at a temperature high enough to achieve an appreciable hardening effect, a considerable amount of scale is formed and the fatigue strength is also reduced. At the other end of the temperature scale, it was subsequently shown that the coefficient of friction of commercially pure titanium markedly decreases when it is heated in air at 350°C for 17 hours; it was also shown that the coefficient of friction of the oxidised

surface of titanium remains low after removal of brittle compound layers (see E.S. Machlin et al, Journal of Applied Physics, Vol 25, 1954 pages 576 to 581 and W.R. Yankee, "Influence of Oxygen and Nitrogen in Solution in Alpha Titanium on the Friction Coefficient of Copper on Titanium", Transactions AIME, September 1954 pages 989 to 990). However, such a procedure is costly since it requires the additional step of removal of such brittle layers.

In view of the difficulties associated with the severe scaling of titanium alloys when heated in air, the possibility of controlled oxidising in molten salts has been investigated. When titanium specimens are heated in lithium carbonate salt baths at temperatures between 600 and 900°C for 2 to 4 hours, satisfactory layers are said to be formed. The technique has been used for the production of batches of titanium pistons, as disclosed by E. Mitchell et al in, "Surface Treatments for Improving the Wear Resistance and Friction Properties of Titanium and its Alloys", Journal of the Institute of Metals, Vol 93 1964/65, pages 381 to 386. Also, JP-A-56-146875 (Patent Abstracts of Japan, Vol 6, No. 24 (C-91) 12 February 1982) discloses the formation of stable titanium oxide on a titanium material by burying the material in magnesium oxide or aluminium oxide and heating at 550 to 850°C in air.

The so-called Tifran process (see A. Goucher et al, "Nouvelles Possibilites de Frottement des Alliages de Titane: Le Tifran," Entropie, No. 63, 1975, pages 36-41) has been used to treat Ti-6Al-4V and involves gaseous oxidation of the titanium alloy at 750°C for 10 hours to produce a case depth of about 50 μm . The process is reported to result in a surface layer having a titanium oxide base, and a diffusion zone. However, such process parameters produce a porous poorly adherent

oxide layer and carry with them the risk that components of complex geometry would be distorted. In another form of the Tifran process, the titanium alloy is oxidised at 630°C for 3 hours. However, this produces a titanium dioxide layer of negligible thickness.

R.M. Streicher et al, "New Surface Modification for Ti-6Al-7Nb alloy: Oxygen Diffusion Hardening (ODH)", *Biomaterials*, Vol 12, 1991 pages 125-129 disclose graded oxygen diffusion hardening to a depth of 50 μm with a maximum hardness of 900 HV compared with 360 HV for the untreated alloy. The ODH-treated alloy is claimed to have improved friction and wear resistance and to be useful in surgical prostheses. The corrosion resistance of the ODH-treated titanium alloy is claimed to be equal to that of commercially pure titanium and the un-treated alloy. However, no parameters are described and the micrographs show no evidence of a TiO_2 layer of a dimension with which the present invention is concerned.

M. Mushiake et al, "Development of Titanium Alloy Valve Spring Retainers", SAE Technical Report Series No. 910428, 1991 pages 41 to 49, disclose a wear-resistant surface treatment based on air oxidation to protect valve spring retainers made of Ti-22V-4Al β titanium alloys. A better wear resistance is said to be afforded to the component by using the oxidation process treatment as compared with either ion nitriding or gas carburising. M. Mushiake et al disclose that oxidation at 850°C for 30 minutes of such titanium alloy valve spring retainers imparts a better wear resistance than that of steel retainers. However, this process is not applicable to α or $\alpha + \beta$ alloys since it alters the bulk microstructure, degrades the properties and risks causing problems of distortion, particularly for components of complex geometry.

WO95/09932 discloses the oxidation of a titanium alloy product to improve tribological properties by a procedure which involves deep surface hardening to a depth of greater than $100\text{ }\mu\text{m}$ by localised surface re-melting without further alloying, optionally surface finishing the deep surface hardened material, oxidising to a depth of less than $100\text{ }\mu\text{m}$ (usually less than $50\text{ }\mu\text{m}$ and preferably in the range of $1\text{-}20\text{ }\mu\text{m}$), followed by modification of residual stress by shot peening or heat treatment. The above treatment improves rolling contact fatigue resistance and scuffing resistance. Thermal oxidation of the alloy product in air at 600 to 850°C produces layers of oxide and oxide-rich Ti at the surface. In one particular example, thermal oxidation in an air-circulation furnace for 10 hours at 650°C is performed as part of the previously described processing sequence which results in a very substantial improvement in wear resistance as compared with the completely un-treated material.

A. K. Mishra et al ("Diffusion Hardening - A New Surface Hardening Process for Titanium Alloys" , Surface Modification Technologies VII, The Institute of Materials, 1994 pages 453 - 471) refer in general terms to a procedure for diffusion hardening a Ti-13Nb-13Zr alloy which involves using a proprietary treatment in an atmosphere containing atomic oxygen, but without giving any process details. Treated specimens are said to have a $0.7\text{ }\mu\text{m}$ surface layer comprised of ceramic oxides such as ZrO_2 , TiO_2 and Nb_2O_5 with an oxygen penetration depth of $2 - 3\text{ }\mu\text{m}$, and an increased surface hardness and abrasion resistance

It is an object of the present invention to provide an improved oxidation treatment which is simple to operate and which can produce titanium or titanium alloys having improved tribological properties such that the

treated material is suitable for use in a relatively wide variety of applications.

According to one aspect of the present invention, there is provided a process for improving the tribological behaviour of a titanium or titanium alloy article, comprising gaseous oxidation of the article at a temperature in the range of 500 to 725°C for 0.1 to 100 hours, the temperature and time being selected such as to produce an adherent surface compound layer containing at least 50% by weight of oxides of titanium having a rutile structure and a thickness of 0.2 to 2 μm on a solid solution-strengthened diffusion zone wherein the diffusing element is oxygen and the diffusion zone has a depth of 5 to 50 μm .

According to another aspect of the present invention, there is provided a titanium or titanium alloy article having (i) an adherent 0.2 - 2 μm thick surface compound layer containing at least 50 % by weight of oxides of titanium having a rutile structure, and (ii) a solid-solution strengthened oxygen diffusion zone having a depth of 5 to 50 μm .

The gaseous oxidation treatment is preferably effected for at least 0.5 hours. It is to be appreciated that, whilst the treatment procedure is within the above specified time and temperature ranges, not all combinations of these times and temperatures will produce the required surface compound layer and oxygen diffusion zone. The gaseous oxidation treatment may be effected for 60 to 100 hours at 580 to 620 °C. For example, such treatment may be effected for about 75 to 100 hours (preferably about 75 hours) at about 600 °C. Alternatively, the treatment may be effected at about 660-700°C for about 0.1 to 8 hours. For example, treatment (a) for about 0.1 to 2.5 hours at about 700 °C

(treatment for 2.5 hours at 700°C produces a surface compound layer having a thickness of about 1 μm and an oxygen diffusion zone having a depth of about 10 μm); or (b) for about 0.1 to 5 hours, preferably about 5 hours at about 680 °C.

The gaseous oxidising atmosphere may be an atmosphere having an oxygen partial pressure of 0.1 to 1. This may be achieved under a reduced pressure or under normal atmospheric pressure. Conveniently, the gaseous atmosphere is air (oxygen partial pressure = 0.2)

More preferably, the surface compound layer has a thickness of 0.5 to 2 μm .

In contrast to WO95/09932, articles which have been oxidised in accordance with the present invention are ready for use without any additional treatment operations thereon.

The invention is applicable to commercially pure grades of titanium and to titanium alloys (α , $\alpha + \beta$, or β alloys). Amongst the titanium alloys which may be used is Ti-6Al-4V. Articles formed of alloys of this type which have been oxidised in accordance with the present invention include valve spring retainers for use in internal combustion engines, e.g. for automotives; balls for ball valves; disks and seats for butterfly valves; domestic and industrial cooking utensils, such as saucepans, frying pans and griddles; and wire ropes. Articles formed of commercially pure grades of titanium oxidised in accordance with the present invention include those listed above apart from automotive valve spring retainers for which Ti-6Al-4V is particularly suited.

In the method of the present invention, the article to be oxidised can simply be placed in a cold or pre-heated furnace and subjected to the specified thermal cycle whilst maintaining a gaseous oxidising atmosphere, e.g. air, in the furnace. Following treatment, the article can be furnace-cooled and is then ready for use without any further treatment.

The treated articles, in addition to having a low coefficient of friction and good resistance to sliding wear against metal or non-metal counterfaces both lubricated and un-lubricated, but especially under lubricated conditions, even with H₂O as the lubricant, are considered to possess good "non-stick" properties.

For certain applications, it may be desirable to subject the resultant treated articles to a *per se* known shot peening operation to improve fatigue properties.

In the accompanying drawings:-

Figs 1 to 6 are graphs showing the properties of untreated testpieces and testpieces treated in accordance with the present invention, and Figs 7 and 8 are optical micrographs of testpieces treated in accordance with the present invention.

In order to demonstrate the advantages of the present invention, titanium alloy testpieces formed of Ti-6Al-4V were placed in a cold furnace containing air and heated for 100 hours at 600°C, followed by furnace cooling. The resultant testpieces will be referred to hereinafter as the "TO treated" testpieces. The TO treated testpieces had a surface compound layer which had a thickness of about 2 μ m and which was

formed mainly of TiO_2 of rutile structure. Below the thin surface compound layer, there was an oxygen diffusion zone forming a hardened layer extending down to a depth of about $15\text{ }\mu\text{m}$. The oxygen concentration of such diffusion zone reduced with depth. These features of the TO treated testpiece will be apparent from Fig 1 which is a graph plotting micro-hardness against distance from the surface in micrometres, and from Fig 2 which is a graph plotting the titanium and oxygen contents in wt% at various distances from the surface in μm .

In nano-indentation tests to assess the mechanical properties of the surface compound layer, the TO treated testpieces had a Hardness Ratio of 2.5, an Elastic Recovery of 40.6 and an E/H ratio of 13.8, as compared with a Hardness Ratio of 1, an Elastic Recovery of 18.3% and an E/H ratio of 26.9 for untreated testpieces. The hardness ratio indicates that the surface compound layer on the TO treated testpieces has a hardness of about 10,000 MPa (approximately 1000 HV). Fig 3 is a graph in which load in mN is plotted against depth in nm for the TO treated and un-treated testpieces. The load versus depth hysteresis curves in the graph of Fig. 3 demonstrate that the oxide layer of the TO treated testpiece exhibits a much shallower penetration depth and a higher elastic recovery compared to the un-treated testpiece.

X-ray diffraction data indicates that the surface compound layer is essentially TiO_2 -rutile.

TO treated and un-treated testpieces were subjected to corrosion tests. Fig 4 shows anodic polarisation curves of the un-treated and TO treated Ti-6Al-4V testpieces and reveals that, after passing through the transition potential, the corrosion currents for both the TO treated and un-treated

testpieces first increase rapidly and then show a passivation stage before rising sharply again. The TO treated testpiece has a lower corrosion current and a more positive transition potential, indicating that it has at least as good a corrosion resistance as the un-treated testpiece, which may be attributed to the dense oxide layer.

Fig 5 shows friction coefficient traces for TO treated and un-treated Ti-6Al-4V testpieces against alumina balls under both oil-lubricated and dry wear conditions. It can be seen that the friction coefficient of the TO treated testpiece is reduced and is more stable than that of the un-treated material both under dry and oil-lubricated wear conditions.

Fig 6 shows wear resistance plotted as weight loss in mg against time in lubricated sliding-rolling wear tests. The steady state wear rates measured in such tests were 1.67×10^{-1} , 9.7×10^{-3} and 9.5×10^{-4} mg/min for un-treated Ti-6Al-4V, an EN19 counterpart, and the TO treated Ti-6Al-4V, respectively. As can be seen from Fig 6, the wear rate of the TO treated testpiece was dramatically reduced by more than two orders of magnitude as compared with the un-treated testpiece and was even lower than that of hardened EN19 steel by a factor of more than 10.

Fig 7 is an optical micrograph of a fracture section of a TO treated testpiece treated as described above where the surface compound layer is indicated by the reference numeral 10 and the substrate is indicated by the reference numeral 12. It can be seen that no delamination has occurred between the surface compound layer 10 and the substrate 12, thus showing that the surface compound layer is adherent and dense.

Fig 8 is another optical micrograph showing the density, adhesion and

uniformity of the surface compound layer 10 on the substrate 12 of the TO treated testpiece.

In a further series of experiments, testpieces of Ti-6Al-4V were TO treated as described above at various temperatures and for various times as shown in the Table below where the oxide layer thicknesses and diffusion zone depths resulting from such treatments are also shown.

TABLE

Run No.	Time (hr)	Temp. (°C)	Oxide Layer Thickness (μm)	Diffusion Zone Depth (μm)
1	50	600	1.4	10.6
2	100	600	2	14
3	3	630	0.2	4
4	10	650	1	8
5	2.5	700	1	10
6*	20	680	8	20
7*	8	700	6	15
8*	20	700	10	27
9*	48	700	15	45

[* - Runs 6 to 9 are given by way of comparison. In each of such Runs, the oxide layer was porous and therefore had insufficient strength to produce adequate tribological properties].

In the above Table, the diffusion zone depth was assessed by examining the response to etching after polishing. The transition between the diffusion zone and the underlying bulk material correlates to a drop of about 10% in hardness which gives a recognisably different response to etching.

In a further series of experiments, small test pieces of butterfly valve discs cast in unalloyed titanium were TO treated as described above at 600 °C for 25, 50, 75 and 100 hours. A load bearing wear test against the TO treated pieces and an untreated test piece showed that all the TO treated samples had an increased load bearing capacity but that the

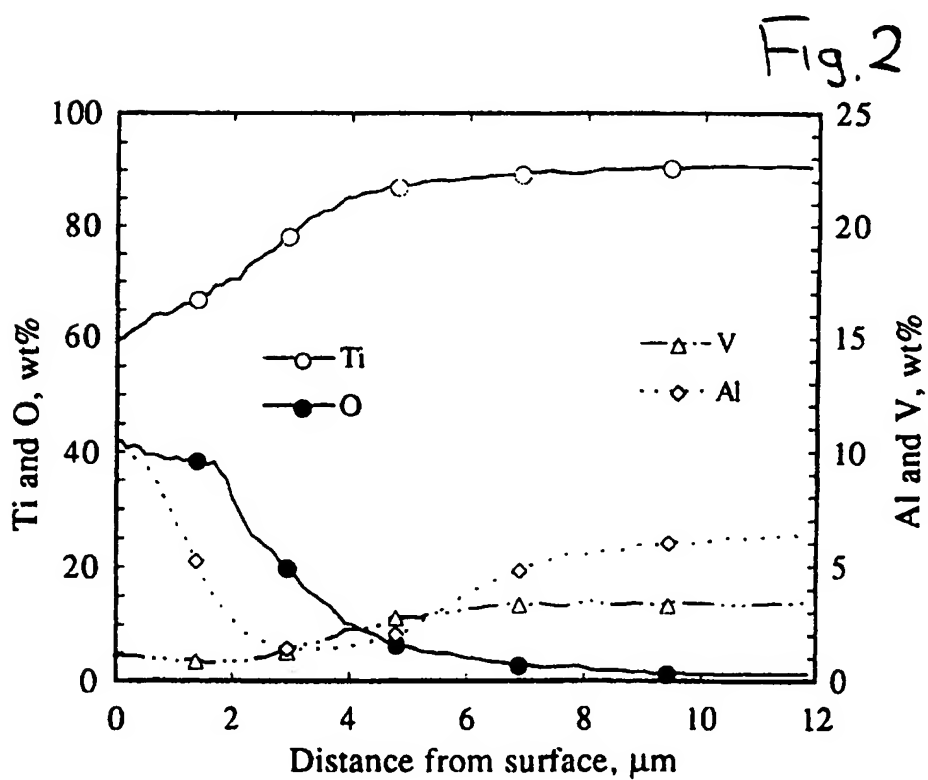
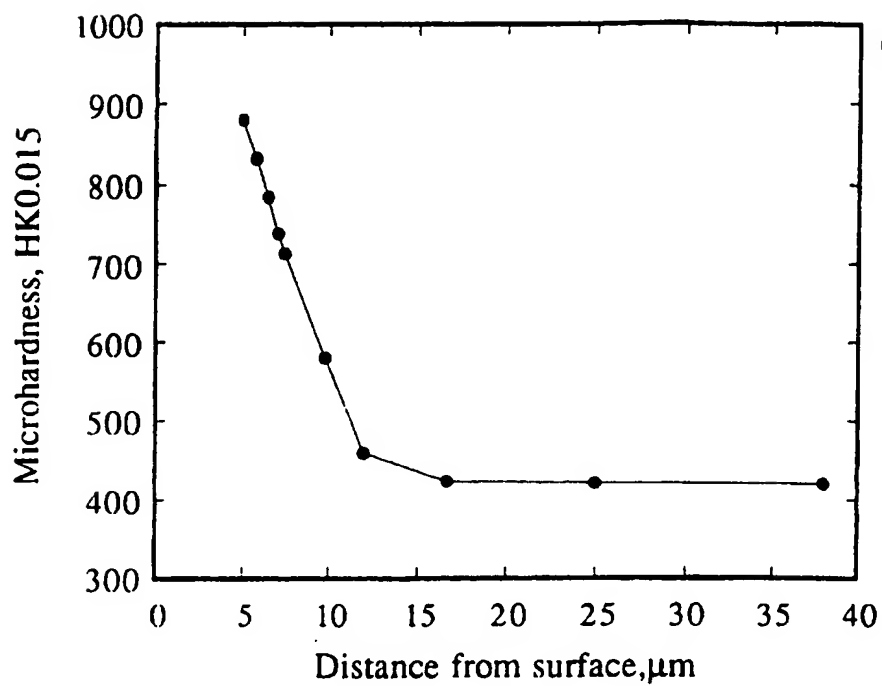
sample treated for 75 hours had the best combination of adherent oxide layer and load bearing capacity.

CLAIMS

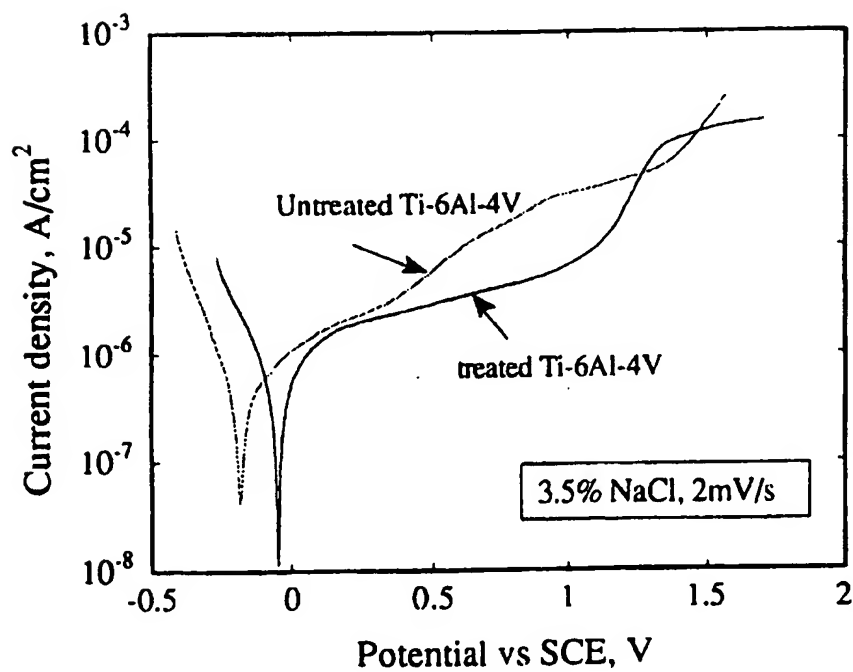
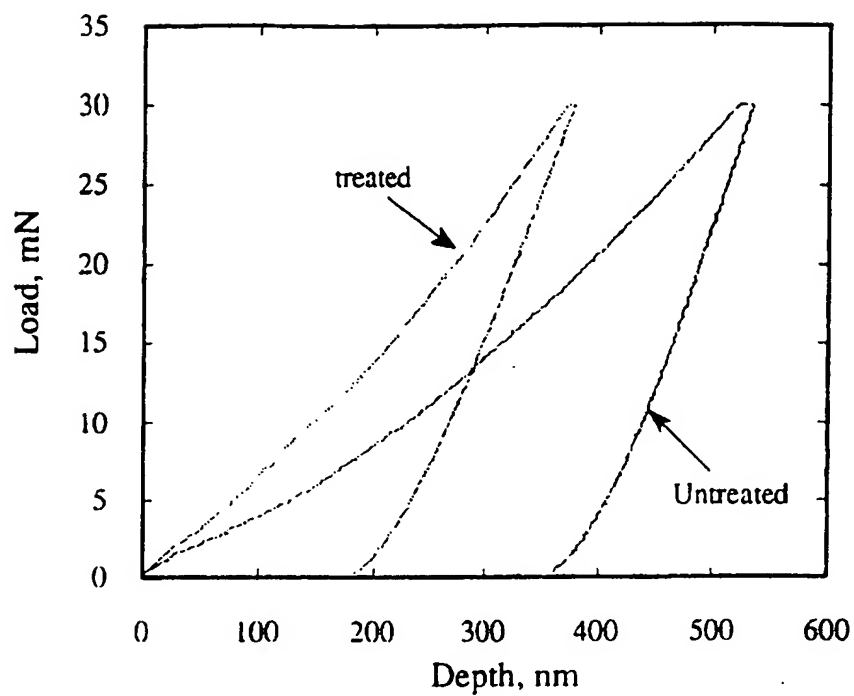
1. A process for improving the tribological behaviour of a titanium or titanium alloy article, comprising gaseous oxidation of the article at a temperature in the range of 500 to 725°C for 0.1 to 100 hours, the temperature and time being selected such as to produce an adherent surface compound layer containing at least 50% by weight of oxides of titanium having a rutile structure and a thickness of 0.2 to 2 μm on a solid solution-strengthened diffusion zone wherein the diffusing element is oxygen and the diffusion zone has a depth of 5 to 50 μm .
2. A process as claimed in claim 1, wherein the gaseous oxidation treatment is effected for 0.5 to 100 hours.
3. A process as claimed in claim 1, wherein the gaseous oxidation treatment is effected for 60 to 100 hours at 580 to 620 °C.
4. A process as claimed in claim 3, wherein the gaseous oxidation treatment is effected for about 75 to 100 hours at about 600°C.
5. A process as claimed in claim 1, wherein the gaseous oxidation treatment is effected at about 660 to 700°C for about 0.1 to 8 hours.
6. A process as claimed in claim 1, wherein the gaseous oxidation treatment is effected for about 0.1 to 2.5 hours at about 700 °C
7. A process as claimed in claim 1, wherein the gaseous oxidation treatment is effected for about 0.1 to 5 hours at about 680 °C.

8. A process as claimed in any preceding claim, wherein the gaseous oxidising atmosphere has an oxygen partial pressure of 0.1 to 1.
9. A process as claimed in claim 6, wherein the gaseous atmosphere is air.
10. A titanium or titanium alloy article having (i) an adherent 0.2 - 2 μm thick surface compound layer containing at least 50 % by weight of oxides of titanium having a rutile structure, and (ii) a solid-solution strengthened oxygen diffusion zone having a depth of 5 to 50 μm .
11. An article as claimed in claim 10, wherein the surface compound layer has a thickness of 0.5 to 2 μm .
12. An article as claimed in claim 10 or 11, formed of a material selected from the group consisting of commercially pure grades of titanium, α -titanium alloys, $\alpha + \beta$ -titanium alloys and β -titanium alloys.

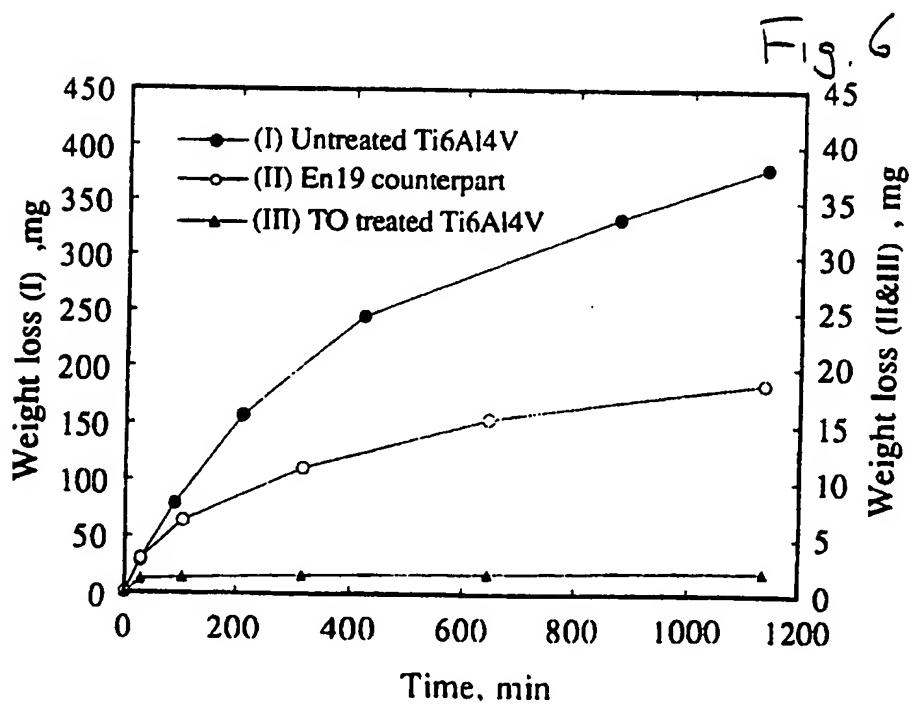
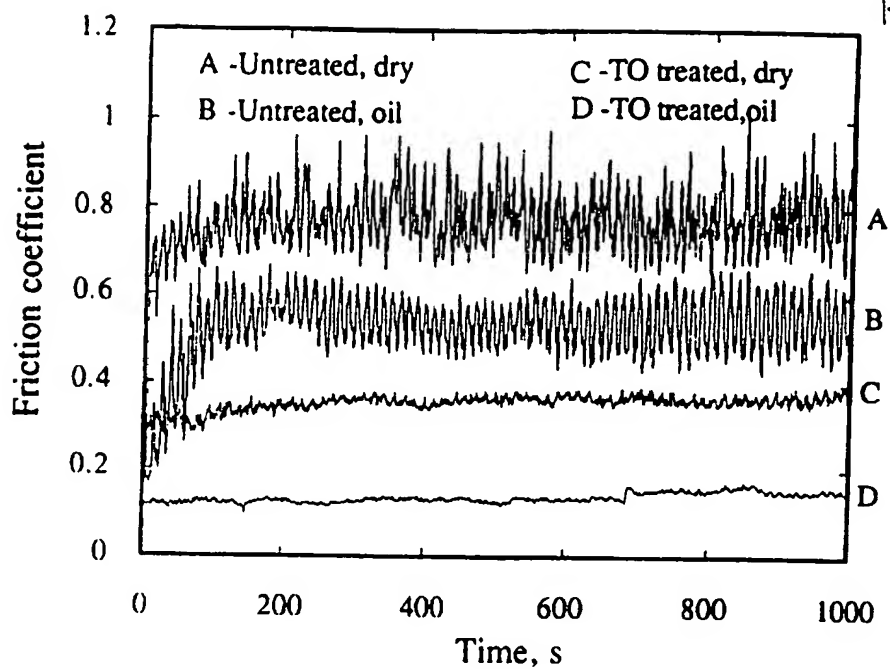
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3/4



4/4

Fig. 7

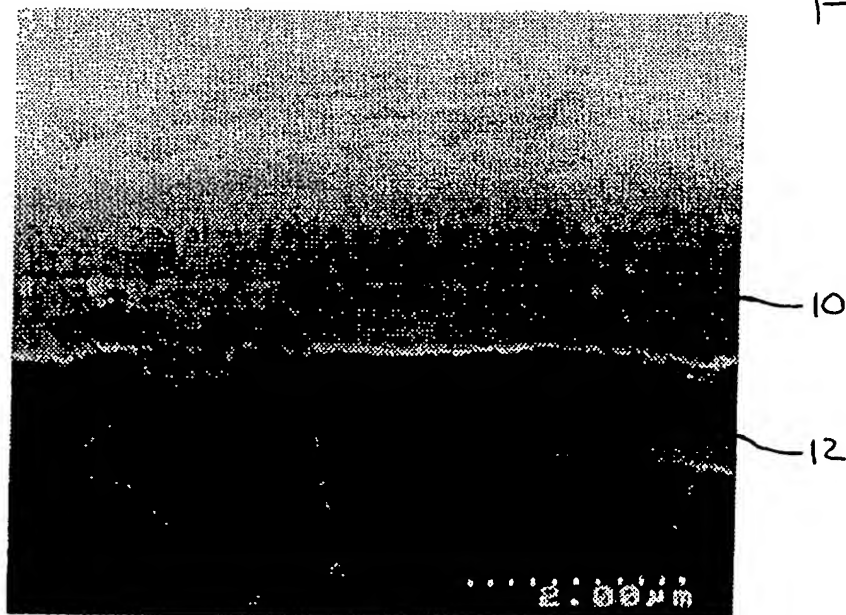
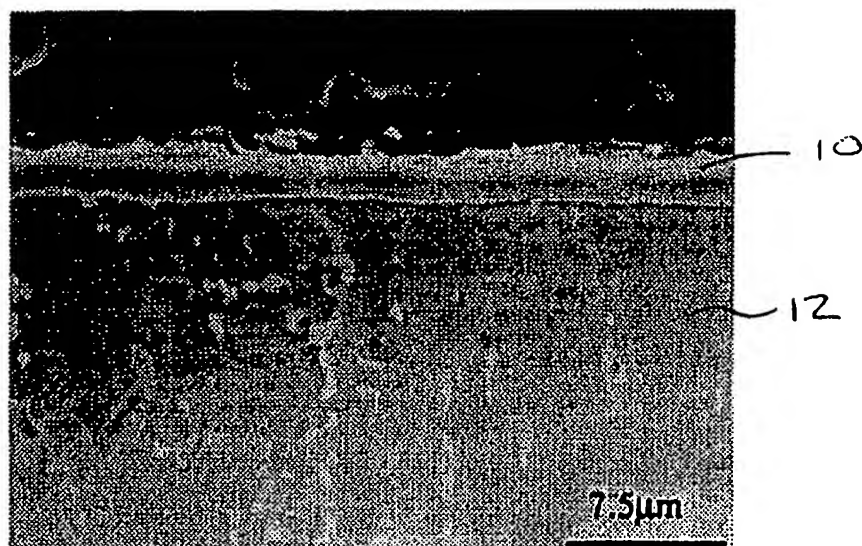


Fig. 8



INTERNATIONAL SEARCH REPORT

Int. Application No.
PCT/GB 97/01902

CLASSIFICATION OF SUBJECT MATTER

IPC6: C23C 8/10, C23C 8/12
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EDOC, JAPIO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

In. ernational application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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